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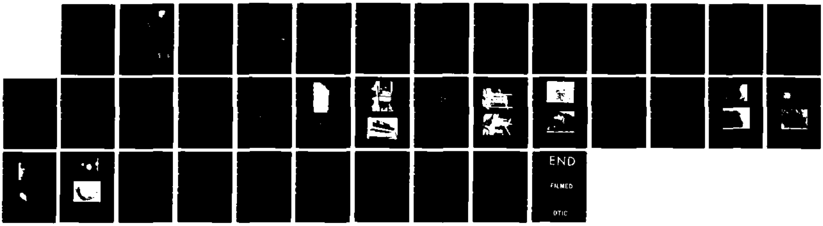

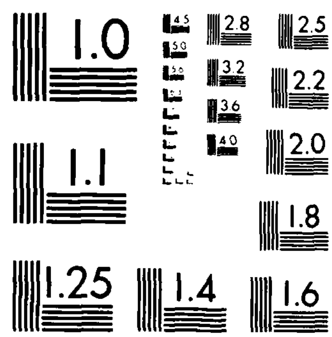

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Final Technical Report
January 1985

PREPARATION OF HEAVY METAL FLUORIDE GLASSES IN THE BULK FORM

SpecTran Corporation

Peter Schultz
Ruth Beni
Richard Kirk

ROME AIR DEVELOPMENT CENTER
Air Force Systems Command
Griffiss Air Force Base, NY 13441-5700

This report has been reviewed by the RADC Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be releasable to the general public, including foreign nations.

RADC-TR-84-279 has been reviewed and is approved for publication.

APPROVED: Martin G. Drexhage

MARTIN G. DREXHAGE
Project Engineer

APPROVED: Harold Roth

HAROLD ROTH, Director
Solid State Sciences Division

FOR THE COMMANDER: John A. Ritz

JOHN A. RITZ
Acting Chief, Plans Office

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A controlled atmosphere glass melting facility has been designed and built at SpecTran. A program has been established to develop a reproducible process for the preparation of high purity, fluoride glasses in the bulk form. A dry-box (< 10 ppm H_2O) has been installed. In addition, a melting furnace has been designed and built. The glasses have been melted under a dry, inert atmosphere, either nitrogen or argon. Both vitreous carbon and platinum crucibles have been used. A black phase has occurred in ten of the first twelve melts. Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy, as well as remelting in CCl_4 have been used to identify the black phase. It has been determined that water and oxygen have leaked into the melting atmosphere and caused cation reduction. With improved furnace seals, five clear melts have resulted. The inert atmosphere process which has been established appears promising, and should be further developed.

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SUMMARY

A controlled atmosphere glass melting facility has been designed and built at SpecTran. A program has been established to develop a reproducible process for the preparation of high purity, fluoride glasses in the bulk form. A dry-box (<10 ppm H_2O) has been installed. In addition, a melting furnace has been designed and built. The glasses have been melted under a dry, inert atmosphere, either nitrogen or argon. Both vitreous carbon and platinum crucibles have been used. A black phase has occurred in ten of the first twelve melts. Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy, as well as remelting in CCl_4 have been used to identify the black phase. It has been determined that water and oxygen have leaked into the melting atmosphere and caused cation reduction. With improved furnace seals, five clear melts have resulted. The inert atmosphere process which has been established appears promising, and should be further developed.

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1.0 INTRODUCTION

The preparation of high optical quality bulk Heavy Metal Fluoride Glasses (HMFG) requires the development of a controlled atmosphere glass melting fabrication facility. These glasses must be batched, melted and annealed in a dry, oxygen free environment. While batching and annealing are commonly done in dry-boxes, there are several approaches that can be taken to the problem of melting these glasses. The anhydrous fluorides can be fused directly in a dry, inert atmosphere, or the raw materials can be melted in a reactive atmosphere such as CCl_4. Several ways to establish an inert atmosphere can be found in the literature. M. Poulain et al have melted fluoride glasses in sealed nickel crucibles.[1-2] An alternate method is to melt under a nitrogen or argon flow.[3-6] The latter method has been used for Phase I of this project for melting zirconium based fluoride glasses. It should be mentioned that the facility can be easily converted to the reactive atmosphere process.

The atmosphere control is a critical problem in fluoride glass preparation, as it is essential to avoid oxide and OH contamination of the raw materials and of the melt. These impurities lead to undesirable mid-IR absorption. Fluorides react with water according to the reaction:

$$\text{Fluorides} + H_2O \quad \text{Oxyfluorides} + HF$$

These compounds can occur in the melt and are not soluble. High concentrations of oxyfluorides in the glass can cause crystallization, making it impossible to obtain a glass.[4] In addition, oxide and OH contamination can lead to the formation of black phases containing reduced cations in the glass.

2.0 PROCEDURE

The glass composition which has been prepared is ZBLAN:

$$55.8ZrF_4-14.4BaF_2-5.8LaF_3-3.8AlF_3-20.2NaF$$

The raw materials used are high purity fluorides, listed in Table 1. The ZrF_4 has been sublimed to remove oxide, lead and carbon impurities. The melts ranged from 30 gms to 140 gms.

Batching has been done in a hermetically controlled glove box (<10 PPM H_2O) to prevent hydrolysis of atmospheric water. The dry-box is a vacuum/atmosphere DL Series, Dri-Lab (Model No. L-001-S-G), with two compartments as shown in Figure 1. Figure 2 shows the gas purification system (HE-493 Dri-Train) used for the dry-box, which includes a molecular sieve and an oxygen getterer. The moisture level in the box is monitored by an AM-2 Moisture Analyzer. The pressure in the box is controlled by the PC-1 Pedatrol, which is equipped with a Photohelic, a combination pressure gauge and differential pressure switch, Figure 3. Finally the dry-box is equipped with a DK-31 Dri-Kool for temperature control within the box, Figure 4.

The glass melting furnace is attached to and accessed through the dry-box, Figure 5,6. It includes a Watlow ceramic fiber heater. Both dry nitrogen and argon have been used as the furnace atmosphere, the glass being melted under a gas flow of approximately 4 LPM. Vitreous carbon and platinum crucibles (50cc and 200cc) have been used together with vitreous and platinum lids. The glass has been heated to 500°C for 1.3 hours, to 850°C for 0.5 hours, and reduced to 650°C before pouring. The molds used are either the vitreous carbon crucible itself or brass and copper slabs. Finally, the glass has been annealed starting at 290°C for greater than 5 hours. This is done in a Thermolyne Furnace (Model no. 1400), which is located within the dry-box.

Glass defect analysis has been done using the ISI SS40 scanning electron microscope, PGT System 4 energy dispersive analyzer, and the American Optical Micro Star polarized light microscope. The glass has been tested for transmission using a Perkin-Elmer 983 infrared spectrometer.

5.0 RESULTS

5.1 Cation Reduction

The first twelve melts of ZBLAN glass have resulted in two clear melts and ten others which contain a black phase. Various atmospheres, temperatures and crucible materials have been tested, but the problem has persisted, see Table II. Melt #1 and #9 are clear, although their success does not correspond to any of the varied parameters.

The SEM/EDS analysis of the black phase does not show carbon (potential contamination from the crucible), see figure 7-9. Furthermore, M. Robinson has demonstrated that if one of these samples containing the black phase is remelted under CCl_4 for one hour, it becomes quite clear and transparent.[7] This suggests that the glass cations are being reduced during the melting process. The black phase can be successfully oxidized, for example $ZrF_{(4-x)}Clx$.[8] These results strongly suggest that the furnace seals have leaked air (O_2, H_2O) in a periodic manner.

With the use of 2 to 4 psi overpressure, and improved upper and lower muffle cap seals, and push rod seal (i.e. the use of a vacuum grease on the viton "O-rings", an improved polish on the push rod surface, and properly sized "O-rings" and glands), the melts are clear. The black phase has been eliminated from the glass, see Table III. Further improvements on the push rod surface should eliminate the slight gray tint which has occurred in melt #13. With use, the push rod surface becomes scratched causing a weakening of the seal. This suggests that there is contact between the two nickel parts, or even abrasion from sublimed ZrF_4.

3.2 Glass Transmission

The IR transmission curve for Melt #15 is shown in Figure 10a, for a sample thickness of .518 cm. The infrared absorption edge begins at 5 m. In addition there is a CO_2 absorption band at 4.2 m, and a water absorption band at approximately 2.9 m, see figure 10b. There is a 2% absorption due to water. Further analysis needs to be done to determine how much of this absorption is due to surface as opposed to bulk water. This will be done in Phase II with Spectran FTIR.

3.3 Glass Defects

As a result of too slow a quenching rate, cyrstallization has occurred in most of the melts. Cubic AlF_3 crystals, 5 m in diameter have been observed both with polarized light and secondary electron microscopy, Figure 11. EDS analysis of polished glass surfaces containing crystals has resulted in the identification of the crystal. These crystals form striation throughout the glass samples.

A second unidentified crystal type has been commonly observed in various melts. Figure 12 shows such a crystal observed in melt #6. The crystal is about 30 m in diameter, appears to be dendritic under the polarized light microscope. (Figure 12a) The SEM analysis of these crystals first found with optical microscopy appear to be clusters of plate shaped crystals. (Figure 12b) The individual crystal is too small for EDS analysis.

Striation can be caused by bubbles. Figures 13 and 14 show this. Bubbles are commonly found on the interface between the glass and the vitreous carbon crucible. Their source is unknown. It is likely that agitation of the crucible during pouring may cause these bubbles to move into the melt.

4.0 CONCLUSIONS AND RECOMMENDATIONS

It has been shown that with care the furnace, which has been designed and built for Phase 1, can be successfully used to melt HMFG in a dry, inert atmosphere. With slight modifications to the furnace, clear fluoride glasses can be successfully melted at SpecTran on a routine basis. In addition, greater care should be taken during pouring and quenching to eliminate defects such as bubbles and crystals.

To Improve Glass Quality:

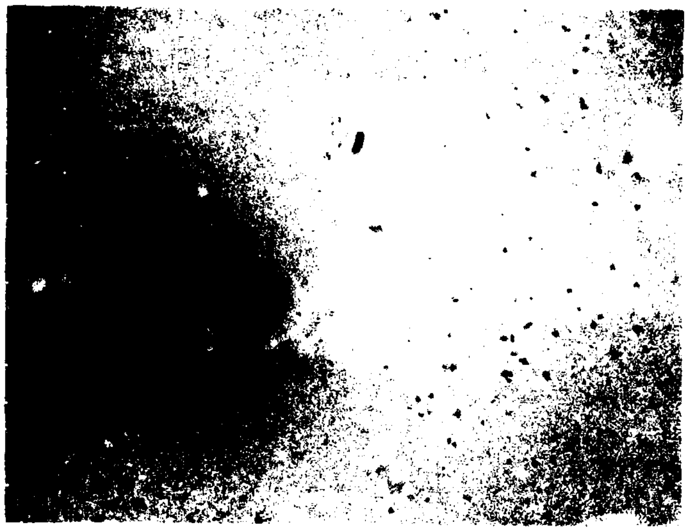
4.1 Atmosphere Control

Improve mushroom seal and automate.

Pressure regulator.

. Oxygen monitor and getter for melt furnace and drybox.

. Modify furnace to allow use of RAP.



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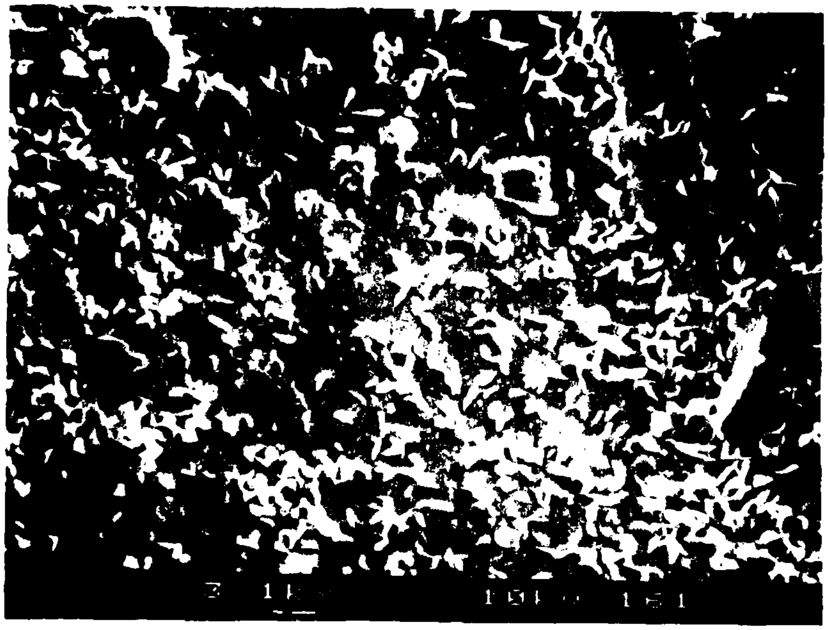

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FIGURE 12

Unidentified Crystal
(a) Polarized Light, 40X; (b) SEM, 3100X

a

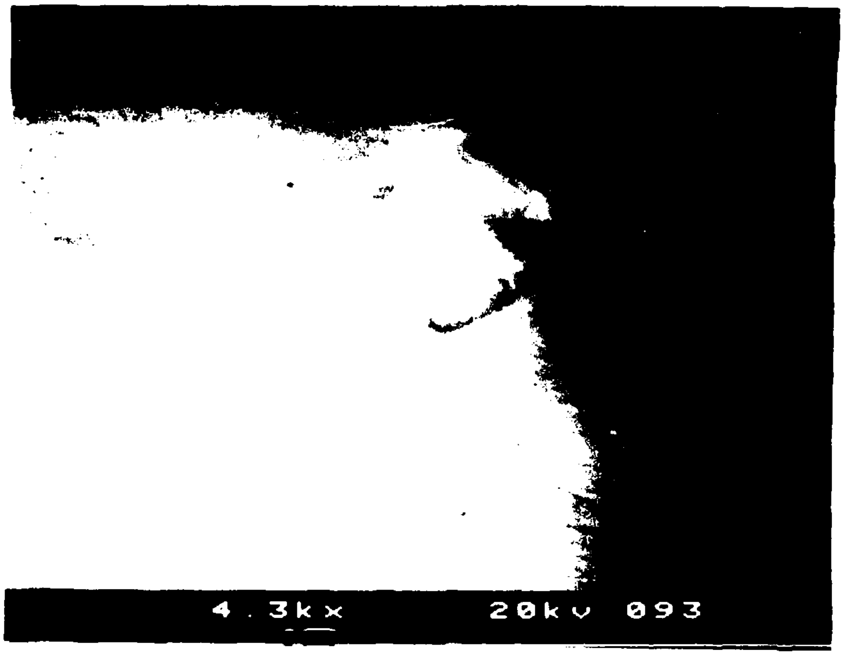

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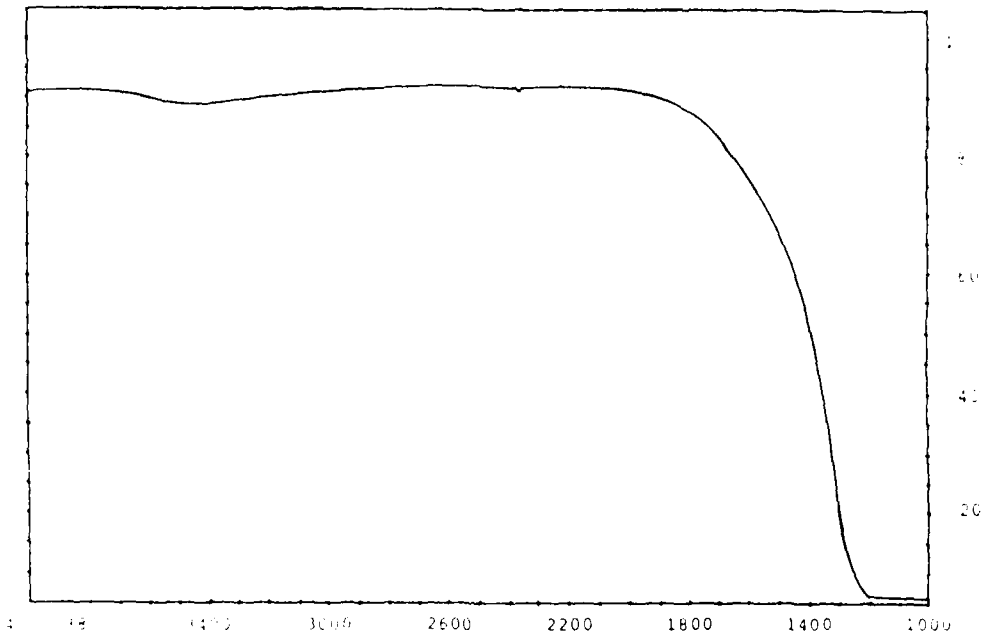
FIGURE 11

Micrograph of AlF_3 Crystals,
(a) Polarized Light, 80X; (b) SEM, 4.3KX.



WAVENUMBER (cm¯1)

FIGURE 10a

Transmission Curve for ZBLAN Glass Remelt #15.

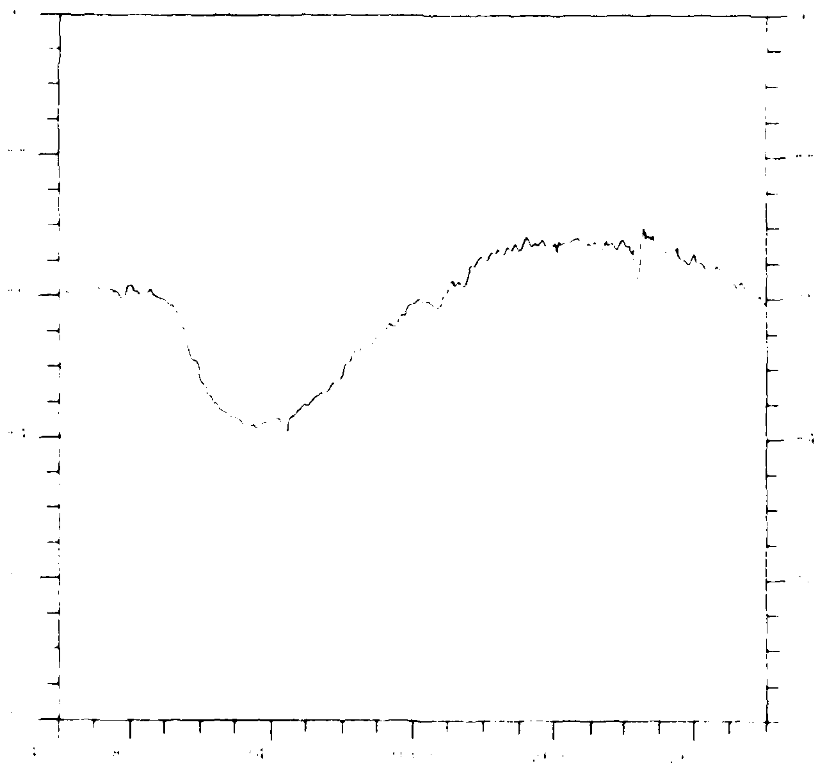


FIGURE 10b

Detail of ZBLAN Transmission Curve Showing the water absorption band.

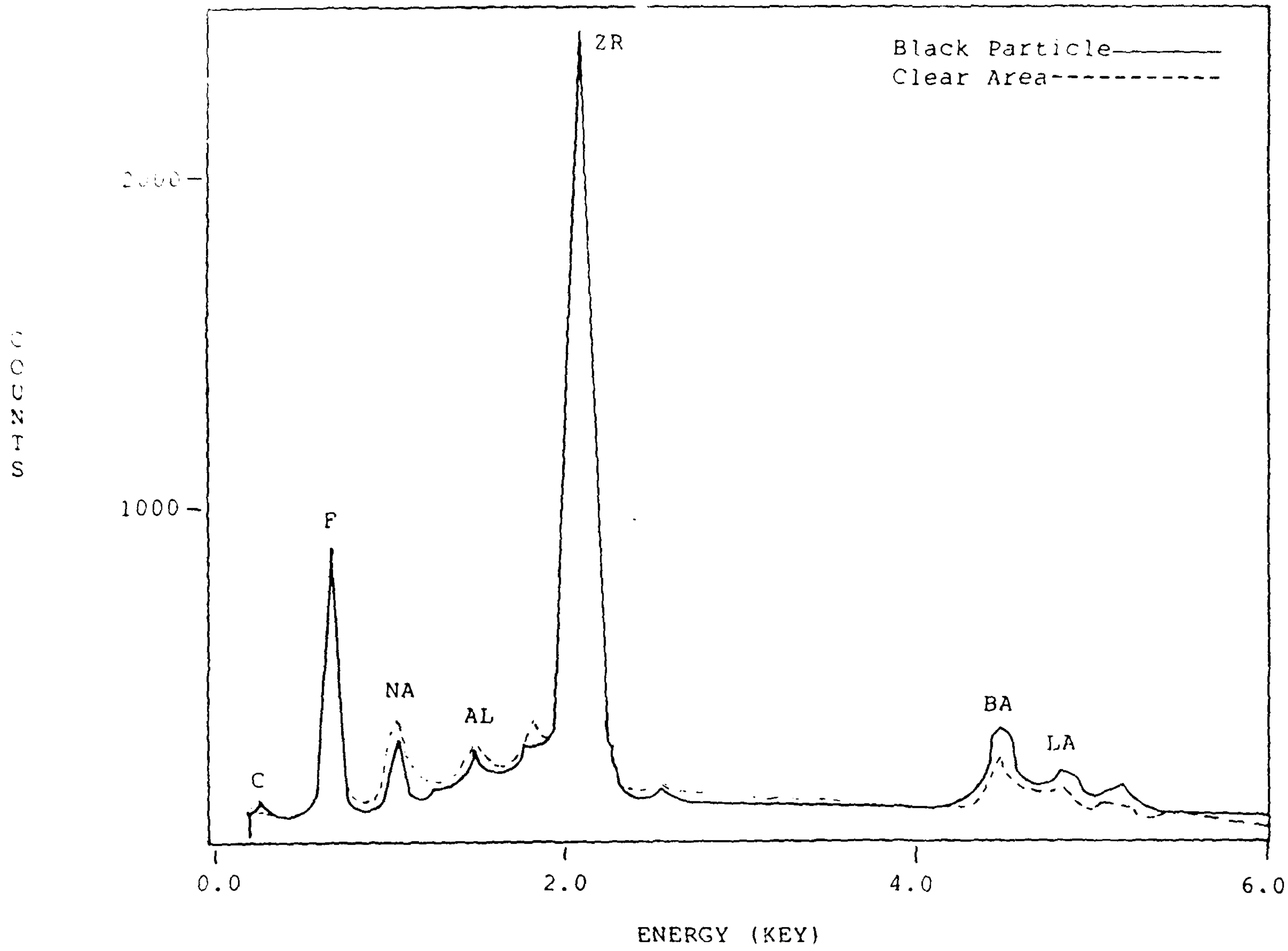


FIGURE 9
EDS Analysis of Black Particulate Versus a
Clear Glass area on the Same ZBLAN Sample.

FIGURE 7

SEM micrograph (BSE) of a polished ZBLAN glass surface containing black particulates.

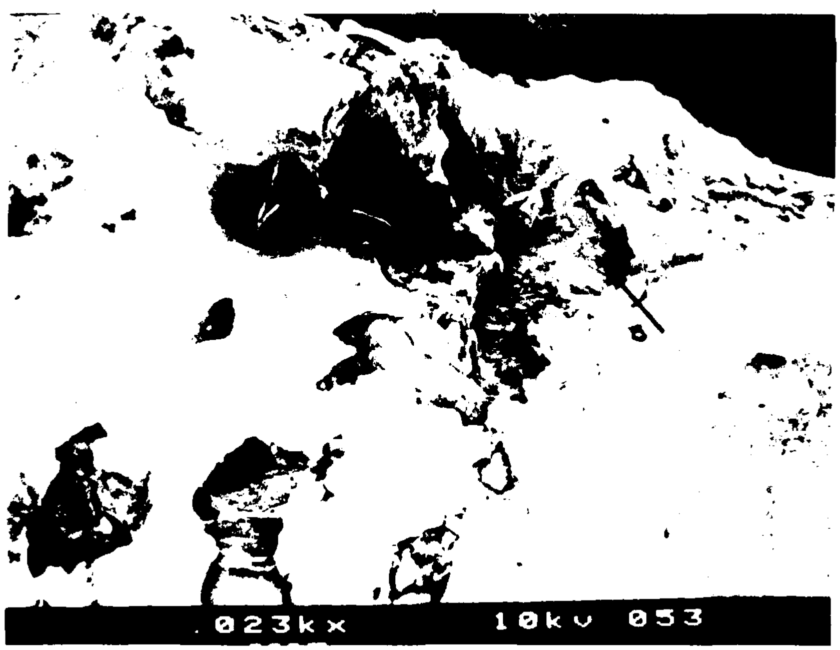


FIGURE 8

SEM micrograph of a fractured ZBLAN glass surface containing black particulates.

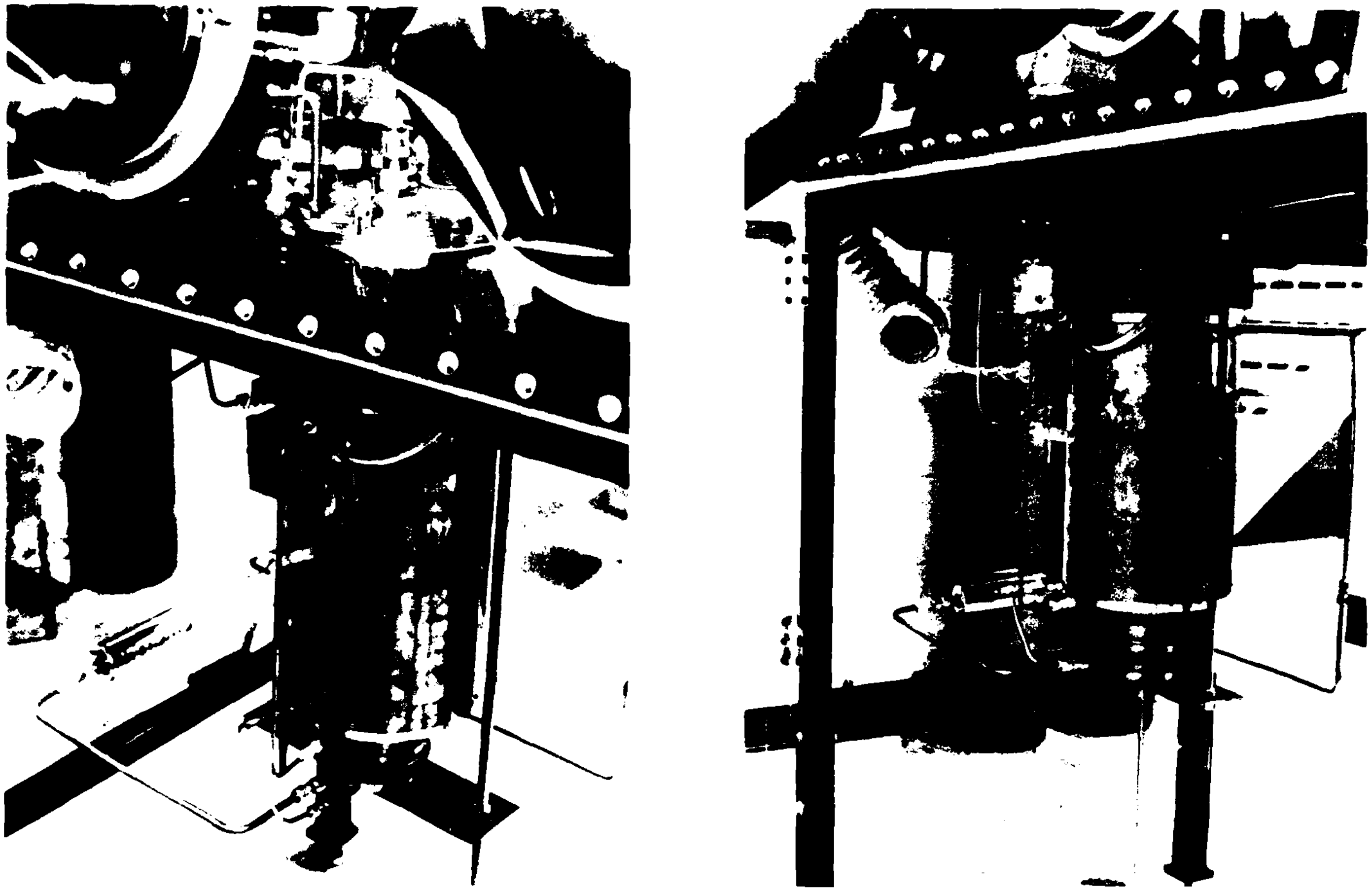


FIGURE 6

Glass melting furnace.

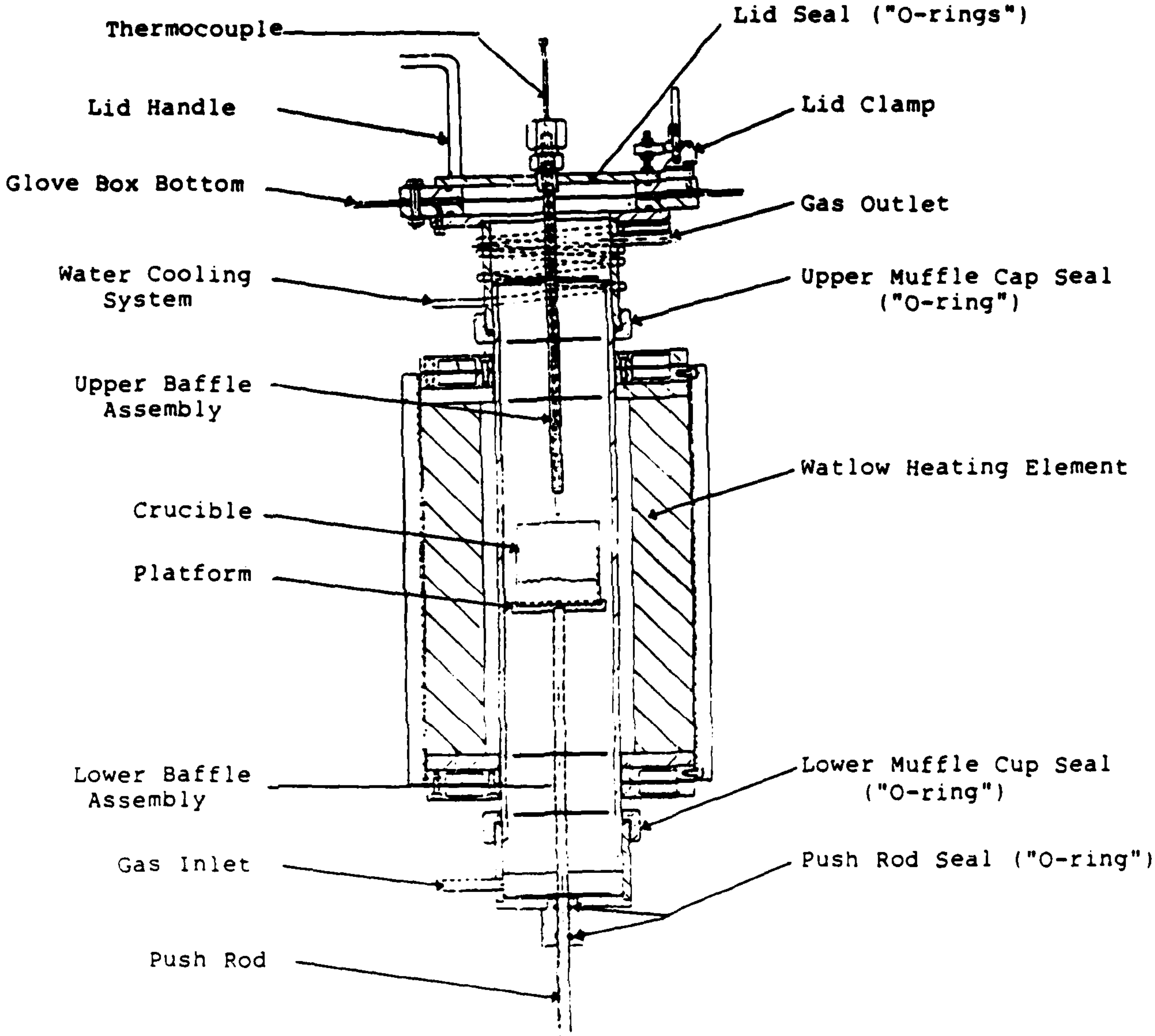


FIGURE 5
Furnace used to melt ZBLAN glass.

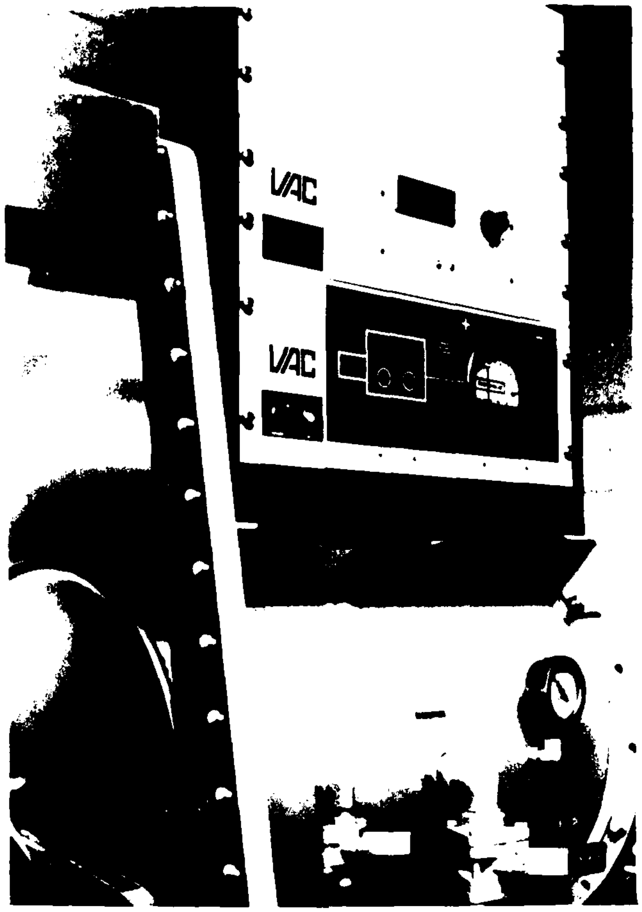


FIGURE 3

Vacuum/Atmosphere Moisture Analyzer
(AM-2), and Pedetrol Panel (PC-1)

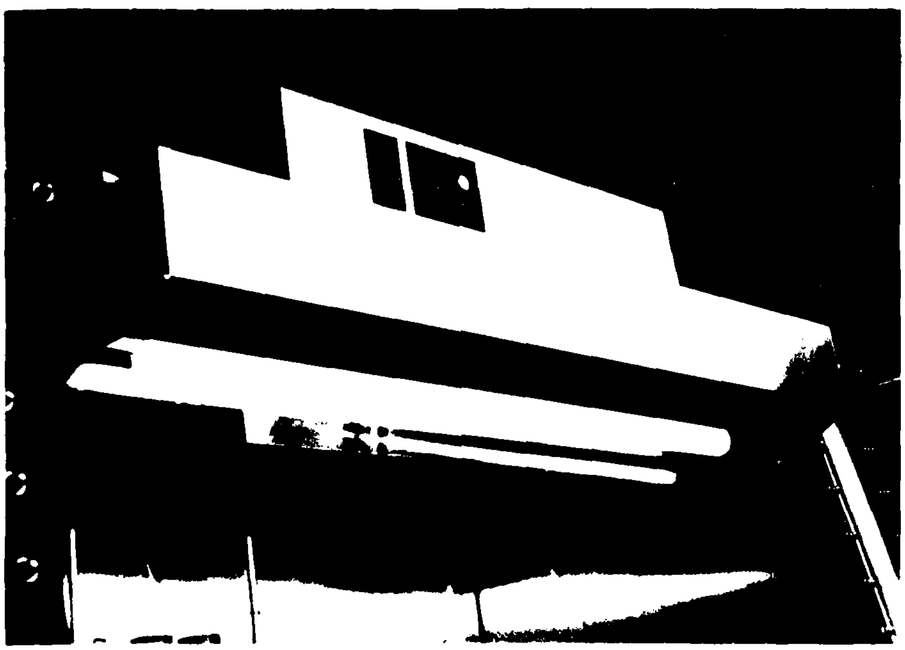


FIGURE 4

Vacuum/Atmosphere Dri-Kool (DK-31)

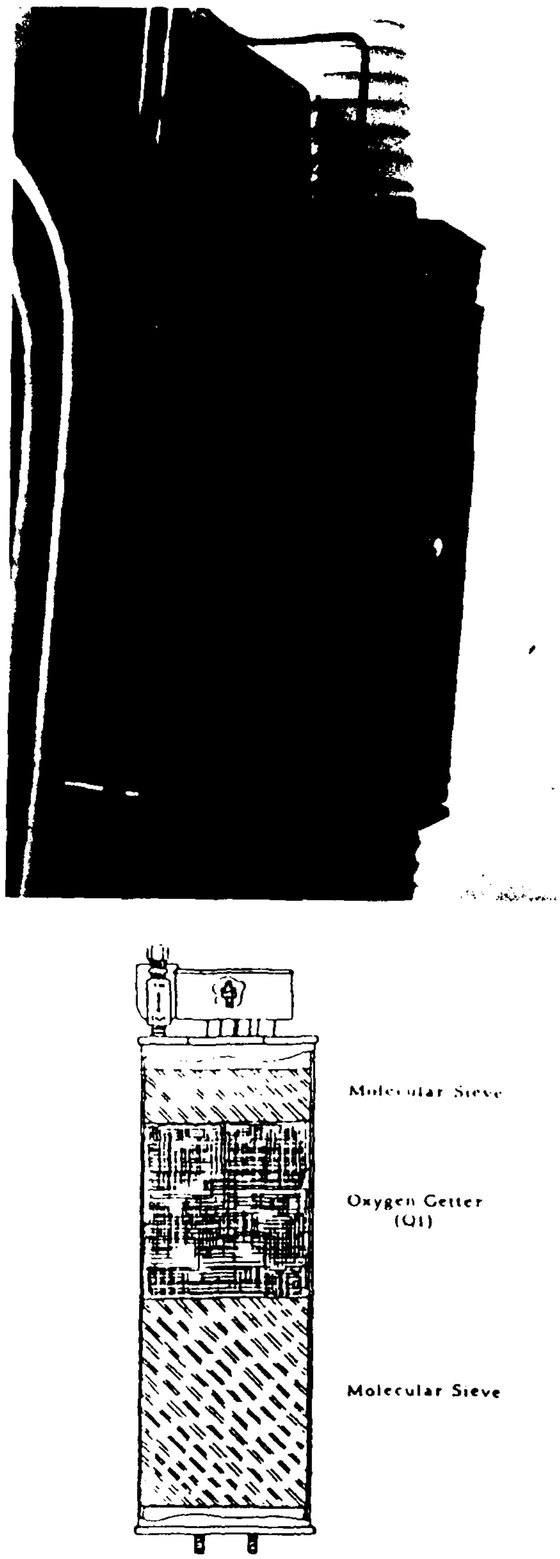


FIGURE 2

Vacuum/Atmosphere HE-493 Dri Train mounted on left end panel of Dri-Lab.

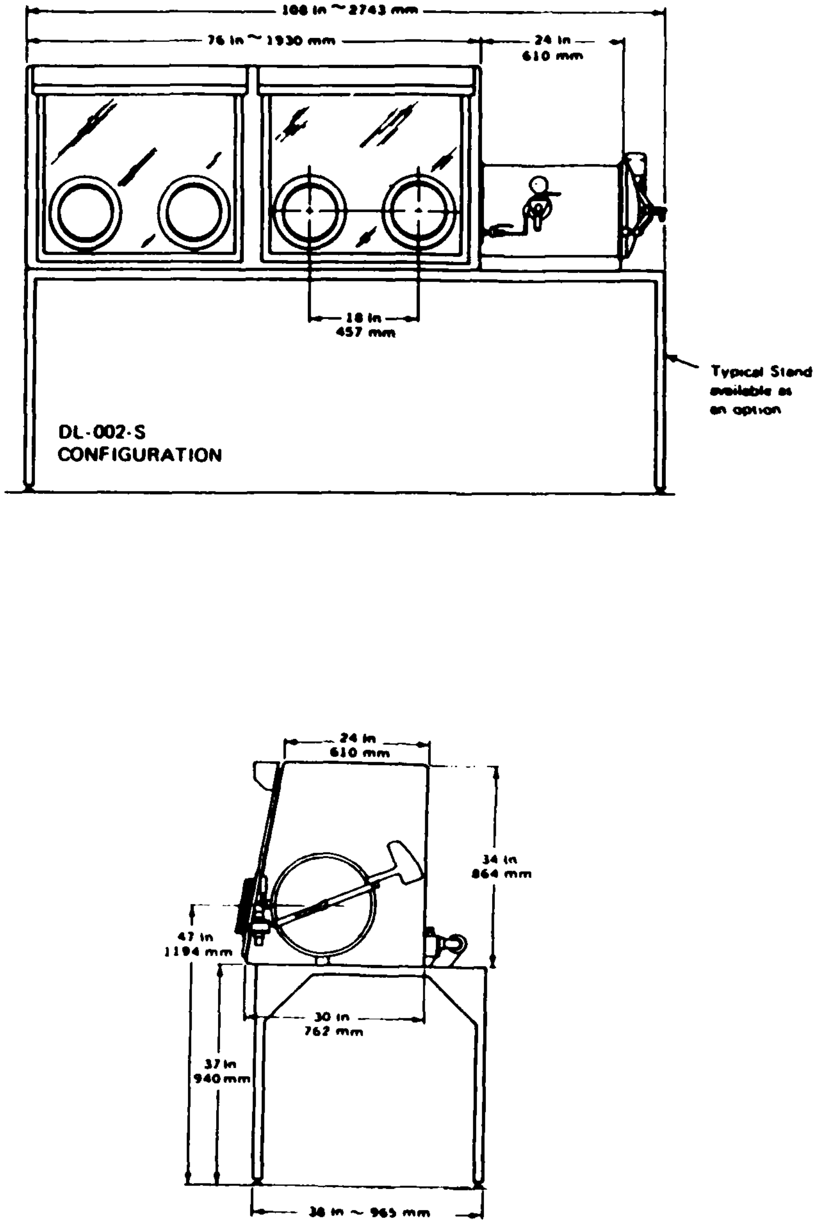


FIGURE 1

Vacuum/Atmosphere DL Series Dri-Lab

Table III

ZBLAN Glass Melts done with the Improved Furnace Seals.

MELT	ATMOSPHERE	OVERPRESSURE	MOLD	RESULTS
13	N_2	2.5PSI	crucible	Clear melt, crystallized on quenching.
(13 remelt)	N_2	2.5PSI	crucible	Clear melt, gray glass with crystals.
14	N_2	2.5PSI	crucible	Lost lid during melt (reduction occurred).
15	Ar	4 PSI	crucible	Clear, crystallized on quenching.
(15 remelt)	Ar	4 PSI	brass mold	Clear glass, with bubbles.

TABLE II

Melt #	Crucible	Atmosphere	Temperature	Results
1	Vitreous Carbon V-25	UHP N_2	810°C	Clear Glass
2	Vitreous Carbon V-25	House N_2	790	Black Particulates in glass
3	Vitreous Carbon V-10	House N_2	790	Black Particulate in glass
4	Vitreous Carbon V-10	House N_2	750	Black Particulates and Crystals in glass
5	Pt	House N_2	780	Incomplete Melt
6	Vitreous Carbon V-25	House N_2 Oxyclear Getter	800	Black Particulates in Gray Glass
8	Vitreous Carbon V-25	House N_2 Oxyclear Getter	845	Black Particulates in Gray Glass
9	Vitreous Carbon V-25	Argon	850 (30 min. soak)	Clear Glass, Crystals formed during annealing
10	Vitreous Carbon V-25	Argon	850 (30 min. soak)	Black Particulates in Gray Glass
11	Vitreous Carbon V-25	UHP N_2	850 (30 min. soak)	Black Particulates in Gray Glass
12	Vitreous Carbon V-25	UHP N_2	850 (30 min. soak)	Gray Glass, with Crystals and Black Particulates

TABLE I

Fluoride	Purity	Source
ZrF_4 (sublimed)*	99.5%	Sassoon Metals & Chemical, Inc.
BaF_2	99.9%	Sassoon Metals & Chemical, Inc.
LaF_3	99.9%	E. M. Chemical
AlF_3	99.9%	E. M. Chemical
NaF	99.9%	Alfa Products

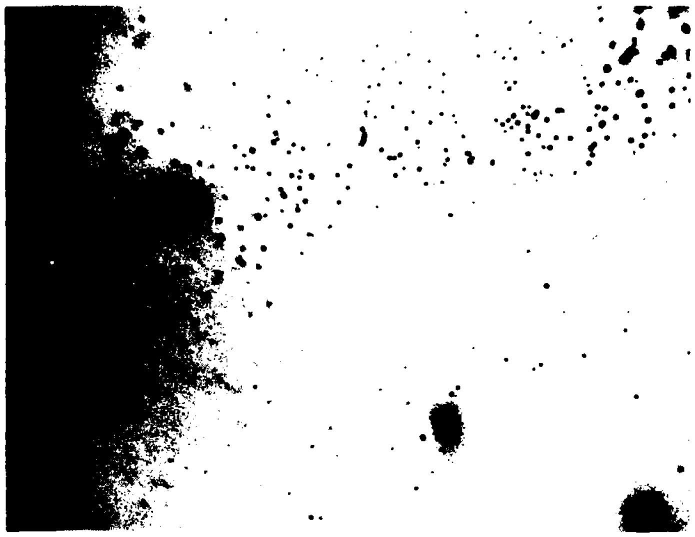
* Prepared at RPI (Moynihan) and HAFB RADC (Suscavage) by heating to 800°C and recondensing at 550°C.

4.2 Melt/Casting Thermal History

- Furnace insulation.
- Program recorder.
- Redesign molds.
- Rotational caster (for preform fabrication).

4.3 Glass Composition

- Modify ZBLAN for core/clad n (eg, NRL Pb doping).
- Try CLAP glasses.



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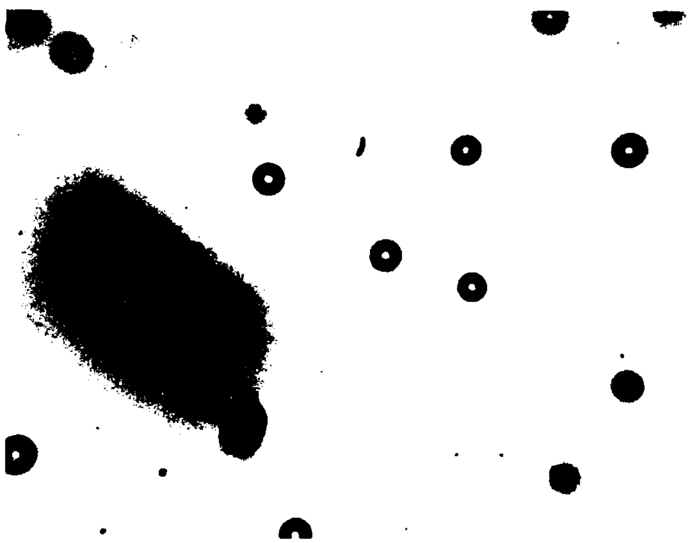

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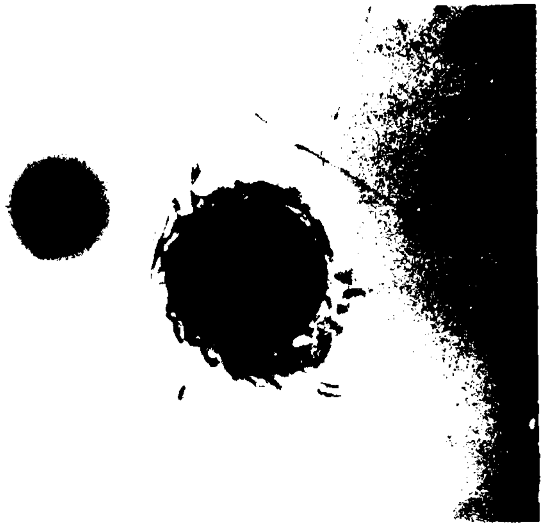
FIGURE 13

Polarized Light Micrographs of Bubbles forming Striation in melt #15
(a) 32X; (b) 80X



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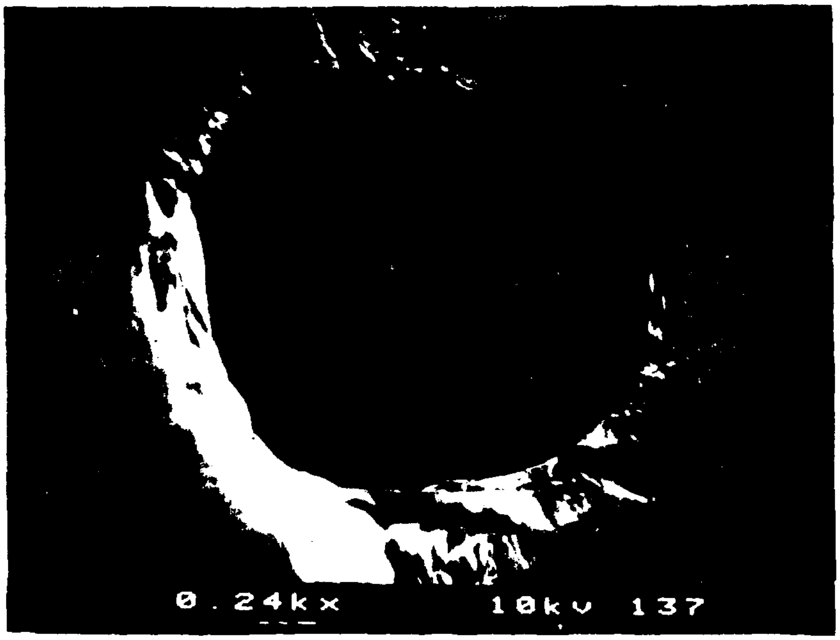

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Figure 14

Micrograph of a Single Bubble Exposed by Surface Polishing of Melt #15
(a) Polarized Light, 50X; (b) SEM 240X

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6.0 PERSONNEL

The following personnel have contributed their efforts to the completion of Phase I.

Ruth Beni, Junior Research Engineer, is responsible for the fluoride glass melting, and the fluoride glass laboratory, in general.

She served previously at Galileo Electro-Optics Corporation as a Research Engineer, until August 1984. At that time, she was involved in developing IR fiber optics, using chalcogenide glasses. Her contribution included the analysis of devitrification and other defects resulting from the fiber draw process, as well as fiber strength analysis, and refractive index profiling.

Before going to Galileo, she studied at Rutgers, where she received her M.S. in Ceramic Engineering and Science, in 1982. There she was concerned with developing a theory to describe the surface structure of pure SiO_2 glass. She also had done glass research on phosphate glasses, which included the following publication:

> R. Beni, W.R. OTT, "Effect of pH on the Durability of Lithuim-Zinc Phosphate Glasses"
> Glass Technology, Vol 22, No 4, 1981.

Brian Caprera, Senior R&D Technician, is currently involved in the Hermetic Coating Project. His responsibilities include; assisting in the construction, development, and operation of the diamond like carbon coating tower and related equipment.

His experience has included the design of high purity gas systems, high temperature furnaces in vacuum and pressure environments. In addition, he has done work in capillary process development, and fiber drawing.

Before coming to SpecTran, he served in the Navy gathering intelligence. He operated both acoustic and nonacoustic intelligence gathering equipment aboard a patrol aircraft, operating such equipment as Magnetic Anomaly Detection Systems, Sonar, Radar, Electronics Counter Measures equipment and IFF Transponding equipment. He assisted in the development of prototype Electronic Counter Measure equipment.

Richard E. Kirk, Analytical Engineer for Research and Development, is responsible for materials analysis for several ongoing projects. He has established and manages an analytical laboratory with SEM/EDS, GC and FTIR capabilities.

He has held the position of Senior Optical Engineer at SpecTran and was responsible for the design, construction and programming of the quality control facility for the testing of optical fiber characteristics including numerical aperture, attenuation and bandwidth.

Mr. Kirk has also held the position of Senior Optical Physicist at Galileo Electro-Optics Corporation, where he was responsible for developing and refining optical fiber measurement techniques. He also developed an index dispersion measurement capability which generated data on fluoride glasses. Also while at Galileo, Mr. Kirk established and supervised an SEM/EDS facility. He was responsible for compositional analysis, fiber characterization and optical properties.

Mr. Kirk is a co-author of a paper on fluoride glass entitled "Material Dispersion of Fluorozirconate-Type Glasses", Appl. Opt., Vol. 20, No. 21, p. 3688.

Mr. Kirk has a Bachelors of Science Degree in Physics from Worcester Polytechnic Institute. He is a member of the Optical Society of America and of Sigma Pi Sigma.

Norman Perazzo, Senior Materials Technician, is currently a consultant at SpecTran. He is presently completing a M.S. program in Materials Engineering at Rensselaer Polytechnic Institute. A resident of Schenectady NY, he earned an Associates Degree in Engineering Science from Broome Community College after a four year enlistment in the U.S. Navy. Following completion of a B.S. degree at R.P.I., he began his thesis work on the electrical conductivity in HMFG under D.C. Moynihan, in May 1983. His work since then has included installation of an enclosed atmosphere system, and implementation of fluoride glass production.

Peter C. Schultz, Vice President of Research and Development, will be the Principal Investigator. He has been actively involved in fiber optics materials and process research since 1968 and is coinventor of the basic patents on doping fused silica fibers and vapor deposition processes. He was part of the original research team that fabricated the world's first low loss optical fiber in 1970.

Prior to joining the SpecTran Corporation, Dr. Schultz was manager of Materials Research at Corning Glass Works, Corning, New York. In this capacity, he led a group of 60 technical personnel and was responsible for all glass research activities in the company, including new optical waveguide materials.

During his 17 years at Corning, Dr. Schultz's personal research involved considerable exploration of doped fused glasses for numerous applications including optical wave guides, bulk optics, semiconductor processing, and space mirrors. He conducted a detailed study of the effect of transition elements on optical transmissions of fused silica as well as a comprehensive investigation of the effect of doped silica fiber composition on radiation response. The latter study was in cooperation with NRL personnel and covered such dopants as Ge, B, P, Ta, Al, Sb, and -OH. He has published over 18 research papers and holds 24 US patents, principally in the field of optical waveguide materials and fabrication.

For his achievements, Dr. Schultz was awarded the first Weyl International Glass Science Award (1977), the SPIE Technology Achievement Award (1981), an IR-100 Invention of the Year Award (1983), Engineering Materials Achievement Award of the American Society for Metals (1983). He is a Fellow of the American Ceramic Society.

Before joining Corning in 1967, he received his BS (1964) and PhD (1967) from Rutgers University in Ceramic Science. Selected publications and patents follow:

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